STUDY ON THE SOLUTION FLUORESCENCE QUenchING FOR POLYSILANES

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Abstract The solution-fluorescence quenching mechanisms of poly (methylcyclohexylsilane), poly (methylphenethylsilane), poly (methylcyclohexylsilane-co-methylphenethylsilane) and poly (methylphenylsilane) are studied by means of steady-state fluorescence, time-resolved fluorescence and UV absorption. The results show that the fluorescence quenching for polysilanes by carbon tetrachloride is the static quenching with energy migration, which is also supported by the qualitative results of the fluorescence quenching behaviors of polysilane by nitromethane (CH₃NO₂) and 2, 4, 7-trinitrofluorenone (TNF).

Key words polysilane; static quenching; energy migration; steady-state fluorescence

1 EXPERIMENTAL DETAIL
1.1 Reagents
PMCS, PMPES, Copolymer and PMPS were synthesized in-house by a Wurtz type reductive condensation of the appropriately substituted dichlorosilane with highly dispersed molten sodium metal. The molecular mass of the polymers were determined by gel permeation chromatography and were based on polystyrene standards, $M_w$: 1.6 $\times$ 10⁶, 2.8 $\times$ 10⁶, 1.8 $\times$ 10⁶ and 1.3 $\times$ 10⁶, respectively.

TNF was prepared by Shanxi University. Hexamethyltetracosane is of gas chromatography grade (imported from Germany). Other reagents and solvents are of analysis grade (Beijing Chemical Plant) and exhibit no fluorescence interference.

1.2 Measurements
Steady-state fluorescence spectra were recorded on Hitachi MPF-4 fluorometer. The lifetime of the fluorescence was determined on a Hiriba NAES-1100 nanosecond fluorometer. Absorption spectra were recorded on a HP-8451A UV-visible spectrometer.

All the experiments were carried out at 20°C unless indicated. For the fluorescence spectra, an excitation wavelength was the maximum absorption wavelength ($\lambda_{\text{max}}$) of the respective polysilane.
RESULTS AND DISCUSSION

2.1 Room-temperature Solution Fluorescence Quenching in PMCS, PMPES, Copolymer and PMPS by Carbon Tetrachloride

For all CC\textsubscript{4} quencher concentrations studied, the ultraviolet absorption spectra of PMCS, PMPES, Copolymer and PMPS in cyclohexane or hexamethyldecacosane solutions remain essentially the same, and they provide no evidence for the formation of any ground state complex between the polymers and CC\textsubscript{4}.

The fluorescence spectra of the polymers are measured in cyclohexane or hexamethyldodecacosane solutions (\(\sim 10^{-4}\) mol\(\cdot\)l\(^{-1}\)). On addition of CC\textsubscript{4} to the polysiulane solutions, the fluorescence intensity of the polymers is gradually quenched, and the peak positions of the emission spectra are invariant. A typical result is emphasized in Fig. 1. The quenching processes of PMCS, PMPES and Copolymer follow the Stern-Volmer equation:

\[
\frac{F_0}{F} = 1 + K_{sv}[Q]
\]

\(F_0, F\) are fluorescence intensity of polysiulanes without adding CC\textsubscript{4} and in the presence of CC\textsubscript{4}, respectively, \(K_{sv}\) is the Stern-Volmer constant, \(\tau_0\) is lifetime of fluorescence, \(K_q\) is quenching rate constant and \([Q]\) is the concentration of the quencher. But the Stern-Volmer plots of PMPS are deviated from Eq. (1), and clearly convex, (Figs. 2 and 3). The fluorescence lifetimes of PMCS, PMPES, and Copolymer in cyclohexane solutions are measured. As the CC\textsubscript{4} concentration increases, the monomer fluorescence lifetime of each polysiulane studied is not changed and decays according to single-exponential kinetics. All the results are listed in Table 1.

As shown in Table 1, the Stern-Volmer constants of PMCS in cyclohexane and hexamethyldodecacosane solutions are almost equal, in spite of the large difference in their shear viscosities. Therefore, the fluorescence intensity quenching of the polymers by CC\textsubscript{4} is not a dynamic one, but a static one.

The \(K_q\) values listed in Table 1 are in a factor of \(10^{10}\) \(\text{mol}^{-1}\cdot\text{sec}^{-1}\), and the values in the usual